

Oxygenated volatile organic chemicals in the oceans: inferences and implications based on atmospheric observations and air-sea exchange models

H. B. Singh¹, A. Tabazadeh¹, M. J. Evans², B. D. Field², D. J. Jacob², G. Sachse³, J. H. Crawford³, R. Shetter⁴, and W. H. Brune⁵

¹ NASA Ames Research Center, Moffett Field, CA 94035

² Harvard University, Cambridge, MA 02138

³ NASA Langley Research Center, Hampton, VA 23665

⁴ National Center for Atmospheric Research, Boulder, CO 80307

⁵ Pennsylvania State University, University Park, PA 16802

Abstract. Airborne measurements of oxygenated volatile organic chemicals (OVOC), OH free radicals, and tracers of pollution were performed over the Pacific during Winter/Spring of 2001. We interpret atmospheric observations of acetaldehyde, propanal, methanol, and acetone with the help of a global 3-D model and an air-sea exchange model to assess their oceanic budgets. We infer that surface waters of the Pacific are greatly supersaturated with acetaldehyde and propanal. Bulk surface seawater concentration of 7 nM (10^{-9} mol L⁻¹) and 2 nM and net fluxes of 1.1×10^{-12} g cm⁻² s⁻¹ and 0.4×10^{-12} g cm⁻² s⁻¹ are calculated for acetaldehyde and propanal, respectively. Large surface seawater concentrations are also estimated for methanol (100 nM) and acetone (10 nM) corresponding to an under-saturation of 6% and 14%, and a deposition velocity of 0.08 cm s⁻¹ and 0.10 cm s⁻¹, respectively. These data imply a large oceanic source for acetaldehyde and propanal, and a modest sink for methanol and acetone. Assuming a 50-100 meter mixed layer, an extremely large oceanic reservoir of OVOC, exceeding the atmospheric reservoir by an order of magnitude, can be inferred to be present. Available seawater data are both preliminary and extremely limited but indicate rather low bulk OVOC concentrations and provide no support for the existence of a large oceanic reservoir. We speculate on the causes and implications of these findings.

1. Introduction

In recent years it has become evident that significant concentrations of a large number of oxygenated organic chemicals (OVOC) are present in the global troposphere [Singh et al., 2001; Wisthaler et al., 2002 and references there in]. These chemicals are expected to play an important role in the chemistry of the atmosphere by sequestering nitrogen oxides (NO_x) in the form of PAN and by providing HO_x free radicals in critical regions of the atmosphere [Singh et al. 1995; Wennberg et al., 1998]. OVOC are believed to have large terrestrial sources (≈ 500 TgC y⁻¹) but our quantitative knowledge about these is rudimentary [Fall, 1999]. Attempts to reconcile atmospheric observations with models have led to the inference that oceans must provide a sizable source of acetone [de Laat et al., 2001; Jacob et al., 2002]. Galbally and Kirstine [2002] have suggested that an extremely large oceanic reservoir of methanol may be present. It is also known that sunlight initiated reactions can decompose organic matter in surface oceans to form a variety of oxygenated chemicals [Zhou and Mopper, 1997]. The role of oceans in the global budgets of OVOC remains largely unexplored and there is little reliable data available. Here we investigate and assess oceanic composition and budget of acetaldehyde (ethanal, CH₃CHO), propanal (propionaldehyde, C₂H₅CHO), methanol (CH₃OH), and acetone (propanone, CH₃COCH₃) based on airborne measurements over the Pacific and models of air-sea exchange. These OVOC are selected because they are among the most abundant and there is reason to believe that they are globally ubiquitous.

2. Results and discussion

During the TRACE-P Spring 2001 experiment, the NASA/DC-8 flying laboratory was used to measure a large number of OVOC in the Pacific troposphere to an altitude of 12 km (Latitude 10-45 °N; Longitude 100-230°E). Complementing these were in-situ measurements of hydroxyl radicals (OH), a key constituent that controls the atmospheric removal rates of OVOC, and multiple tracers of pollution (e. g. CO, C₂Cl₄). Additionally, spectral radiometers were employed to determine photolytic loss rates of the OVOC of interest in the troposphere. More information about measurement methods, mission payload, and flight profiles can be found in the overview paper by Jacob et al. [2003] and references there in.

All of the data discussed here were collected over open oceans some 500-km or more away from the Asian continent. A “pollution filter” based on CO and C₂Cl₄ distribution was employed to mitigate the effects of pollution and is described in more detail in Singh et al. [2003]. This filter eliminated all major pollution influences and resulted in mean tropospheric mixing ratios of 102(±20) ppb/CO and 3(±1) ppt/C₂Cl₄, and is assumed to represent near-background conditions. All analysis in this paper is based on this filtered data set. The observed vertical distribution of the four-selected OVOC under these clean conditions is shown in Figure 1.

It is evident from Figure 1 that measured mixing ratios of acetone and methanol are lower in the marine boundary layer (MBL) compared to the free troposphere, while the reverse is the case for aldehydes. In Table 1 we present mixing ratio data in the MBL (0-2 km, d_{MBL}) and over it (2-4 km) for the OVOC of interest in this study. Figure 1 also shows these mixing ratios simulated along the TRACE-P flight tracks by the GEOS-CHEM global tropospheric model. More details about the GEOS-CHEM model can be found in Jacob et al. [2002]. An in-depth analysis of the atmospheric distribution and global budgets of the large suite of OVOC measured during TRACE-P is being presented elsewhere [Singh et al., 2003].

2.1 Ocean flux

Oceanic fluxes are estimated assuming a steady state behavior in which the entrainment at the top of the MBL, production and losses within the MBL, and net oceanic fluxes are in balance. The various flux terms are described in equations 1-3.

$$F_t = V_e \times \Delta C \quad (1)$$

$$F_{\text{MBL}} = F_{\text{MBL}} (\text{production}) - F_{\text{MBL}} (\text{loss}) \quad (2)$$

$$F_o = - F_{\text{MBL}} - F_t \quad (3)$$

Where F_t is the flux at the top of the MBL, F_{MBL} is the net flux associated with chemical production and loss of OVOC in the MBL, and F_o is the calculated net oceanic flux. A mean entrainment velocity (V_e) of 0.4 cm s⁻¹ is used in all these calculations [Faloona et al., 2003]. To avoid biases due to scatter in the data, gradient across the top of the MBL (ΔC) are determined by using median concentration differences between the 0-2 km and 2-4 km layers. The calculated value of F_t for each OVOC is presented in Table 1.

Since OVOC are both produced and destroyed in the atmosphere, F_{MBL} is a measure of net chemical flux in the MBL. Loss rates in the MBL are calculated assuming that chemical loss is due to reaction with OH and photolysis $\{F_{\text{MBL}} (\text{loss}) = C_{\text{MBL}} \times d_{\text{MBL}} \times (k_i [\text{OH}]_{\text{MBL}} + j_i)\}$. The OH reaction rate constants (k_i) for all species in this study were taken from the compilations of Atkinson et al. [2002]. Diurnally averaged OH_{MBL} concentrations of 1.5 x 10⁶ molec. cm⁻³ were derived from the in-situ OH measurements on board the DC-8 and were also in good agreement with GEOS-CHEM model simulations. Photolytic loss rates (j_i) were directly calculated from spectral radiometric measurements. Combined first order loss rates are shown in Table 1.

The OVOC production in the MBL is primarily determined by the concentrations of specific precursors and OH radicals. In the case of acetone and methanol, the main photochemical formation pathways involve oxidation of propane/i-butane and methane, respectively. An acetone yield of 0.8 from the propane/OH reaction was used [Atkinson et al., 2002]. A methanol mean molar yield of 0.035 from methane oxidation was derived from the GEOS-CHEM model for the 0-2 km region. Median MBL mixing ratios of propane (+i-butane) and methane were 76 ppt and 1772 ppb, respectively. For aldehydes, which are intermediate products of many hydrocarbons, we have used the chemical production rates as calculated by the GEOS-CHEM model. The net MBL flux values due to chemistry (F_{MBL}) are summarized in Table 1.

The net oceanic flux estimates (F_o) are positive (source to the atmosphere) for aldehydes and negative (sink) for methanol and acetone (Table 1). It is also evident that aldehyde fluxes are extremely large in comparison to methanol and acetone. These flux estimates are valid for the Pacific region and are

not likely to be representative of the global oceans. As a first approximation however, if Table 1 fluxes are extrapolated to global scales, an oceanic source/sink (Tg y^{-1}) of 125, 45, -8, and -14 can be calculated for CH_3CHO , $\text{C}_2\text{H}_5\text{CHO}$, CH_3OH , and CH_3COCH_3 , respectively. The finding of an oceanic sink for CH_3OH and CH_3COCH_3 is contrary to previous suggestions of a sizable oceanic source [de Laat et al., 2001; Jacob et al., 2002; Heikes et al., 2002]. As can be seen from Figure 1 (d), a 13 Tg y^{-1} net oceanic source of CH_3COCH_3 in the GEOS-CHEM model greatly over predicts MBL mixing ratios. Similarly an assumed methanol oceanic sink of 15 Tg y^{-1} provided a reasonable fit to the observations (Figure 1c). While these results must be considered preliminary at this stage, they provide the first indications of the important role that oceans could play in the global budgets of OVOC.

Here it is appropriate to add that CH_3OH , and CH_3COCH_3 are relatively long-lived (≈ 2 weeks) and their global concentration fields are reasonably well established [Singh et al., 1995; 2001; de Laat et al., 2001; Wisthaler et al., 2002]. While similar data for short-lived (< 1 day) aldehydes are not available, CH_3CHO mixing ratios in the MBL of 70-400 ppt, indicated by the shaded area in Figure 1a, have been reported from many regions of the globe in both hemispheres [Singh et al., 2003 and references there in]. No data for $\text{C}_2\text{H}_5\text{CHO}$ are available, but its mixing ratios are found to be strongly correlated with CH_3CHO ($R^2 = 0.9$) and it is expected to behave similarly. The ensemble of these observations supports the view that substantial aldehyde concentrations are present throughout the globe. We note that the large oceanic emissions of aldehydes estimated in Table 1 are insufficient to account for their mixing ratios in the free troposphere [Singh et al., 2003].

2.2 Sea water concentrations

To explore oceanic budgets of these OVOC we use a two-film model of air-sea exchange described by Liss and Slater [1974] and further discussed by Donelan and Wanninkhof [2001]. Based on this model, equations 4-5 were used to derive surface seawater concentration and saturation (1+S) necessary to maintain the oceanic flux, F_o .

$$F_o = K_l (C_l - C_g/H) = (1/\alpha k_l + 1/Hk_g)^{-1} (C_l - C_g/H) \quad (4)$$

$$S = HC_l/C_g - 1 = HF_o/K_l C_g \quad (5)$$

where C_l and C_g are concentrations in the bulk liquid and gas phases, H (C_{sg}/C_{sl}) is the intrinsic dimensionless Henry's law constant, k_l and k_g are exchange constants for liquid and gas phases, and α is an enhancement factor due to species reaction in solution. For both aldehydes a hydration constant $\{[\text{RCH}(\text{OH})_2]/[\text{RCHO}]\}$ of 1.4 was used [Zhou and Mopper, 1997 and references there in]. Dimensionless intrinsic Henry's Law constants shown in Table 2 were obtained from the data compiled by Sander [1999] and corrected for the reduced solubility in sea water ($\times 1.2$) and in case of aldehyde for hydration effects ($\times 2.4$). A liquid phase exchange constant (k_l) of 11 cm h^{-1} and a gas phase exchange constant (k_g) of $6912 (18/\text{MW})^{1/2} \text{ cm h}^{-1}$ was used based on recommended values for a mean surface wind speed of 6 m s^{-1} [Donelan and Wanninkhof, 2001, Asher, 1997]. These calculations are relatively insensitive to α , which is calculated to be 2.0 for aldehydes and 1.0 for other OVOC according to Liss and Slater [1974].

As can be seen from Table 2, both gas phase ($r_g = 1/Hk_g$) and liquid phase ($r_l = 1/\alpha k_l$) resistances are important to the air-sea exchange of OVOC. Air-sea exchange models have been predominantly validated for sparingly soluble and relatively inert species (such as O_2 , N_2 , N_2O , and CO_2) where the liquid phase resistance dominates. Reactive organic chemicals such as OVOC as well as chemicals for which resistance to transfer resides principally in the gas phase have not been extensively studied. Given these caveats, equation 4 is used to calculate bulk surface seawater concentrations ($10^{-9} \text{ mol L}^{-1}$ or nM) of 7, 2, 100, 10 for CH_3CHO , $\text{C}_2\text{H}_5\text{CHO}$, CH_3OH , and CH_3COCH_3 , respectively (Table 2). A comparably large concentration of the hydrated ion of CH_3CHO and $\text{C}_2\text{H}_5\text{CHO}$ would also exist in seawater. These results indicate a very large seawater super-saturation of aldehydes. In comparison, Pacific waters appear to be under-saturated in methanol (6%) and acetone (14%) and provide a modest net sink. This sink corresponds to a deposition velocity (SK_l/H) of 0.08 cm s^{-1} methanol and 0.10 cm s^{-1} acetone.

Bulk surface concentration (C_l) typically represents the top 50-100 m well-mixed region of the oceans [Kantha and Clayson, 2003]. Assuming a 50 m mixed layer, the oceanic loading of these species over the Pacific can be calculated to be 2-25 times their atmospheric loading (R in Table 2). Adjusting for hemispheric differences and extrapolating to global scales, a very large oceanic reservoir of these species ($\approx 65 \text{ Tg}$) can be calculated to be present (Table 2). In their assessment of the global budget of methanol, Galbally and Kirstine [2002] assumed saturation in the top 80 m to calculate an oceanic methanol reservoir

some 66 times larger than the atmospheric reservoir. Heikes et al. [2002], in an independent review of the methanol budget, estimate a methanol oceanic source of 0-80 Tg y⁻¹ but did not imply a reservoir.

Is there evidence for the large oceanic concentrations and the implied reservoir of OVOC estimated in Table 2? Two studies provide some preliminary indications. In the first study, Zhou and Mopper [1997] use a wet chemical technique to measure CH₃CHO and CH₃COCH₃ in coastal and open ocean areas east of Florida. They report a bulk seawater concentration range of 1-15 nM for CH₃CHO and 3-15 nM for CH₃COCH₃. Bulk water concentrations in two open ocean samples collected from a location some 100 km east of Bahamas were 1 nM for CH₃CHO and 3 nM for CH₃COCH₃. However, the concentrations in the surface microlayer ($\approx 10^2$ μ m) were 10-20 times larger. In a more recent investigation, using a sensitive mass spectrometric technique, Williams et al. [2003] report bulk seawater concentrations of <1 nM for CH₃OH and CH₃COCH₃ in the open tropical Atlantic ocean. They also find that these low concentrations are nearly uniform in the top 50 m of the ocean. The atmospheric mixing ratios measured by them were similar to those in Table 1. The available oceanic data at the moment are preliminary and too limited to draw any firm conclusions. However, they do indicate that bulk seawater concentrations in remote oceans for several of these OVOC may be much lower than predicted by current air-sea exchange models (Table 2). These limited measurements provide no direct support for the presence of a large OVOC oceanic reservoir.

The super-saturation of aldehydes and under-saturation of acetone are indicative of the fact that the OVOC are being produced and destroyed in the oceans. We know little about these mechanisms. Formation processes could involve photo or biodegradation of organic matter. It is also possible that high OVOC concentrations inferred in Table 2 are present only in surface microlayers over the ocean [Zhou and Mopper, 1997]. For species such as aldehydes, where oceans are a source, a steady flux can be maintained from deep reservoirs but thinner layers must be continuously replenished if they are not to be quickly depleted. This almost certainly requires a mechanism for near-continuous OVOC formation in seawater. If these processes are driven by the availability of sunlight, then strong diurnal variations should be expected. Similarly, loss processes in seawater could include rapid consumption by bacteria, typically present in the top few meters, as well as photodegradation. At the moment it is not possible to reconcile the expected results from air-sea exchange models with the extremely limited and somewhat preliminary available oceanic data.

3. Conclusions

In this study we have used atmospheric measurements of OVOC and a standard air-sea exchange model to explore their oceanic budgets. Current models suggest that oceans should contain a very large reservoir of OVOC and may provide a net source in some cases and a sink in others. However, the reliability of these models for reactive organic species remains untested. Available observational data are extremely limited and uncertain. Mechanisms for the formation and destruction of OVOC in seawater are largely unknown. There is clearly an urgent need for more research on the abundance and fate of OVOC in the oceans. The development of reliable air-sea exchange models for reactive and moderately soluble organic species is also a worthwhile long-term objective.

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Table 1: OVOC mixing ratios and there oceanic flux under pristine conditions

Parameters ^a	CH ₃ CHO	C ₂ H ₅ CHO	CH ₃ OH	CH ₃ COCH ₃
Median Mixing ratio (0-2 km)	205 (204±40) ^c	60 (68±24)	563 (575±211)	437 (466±97)
Median Mixing ratio (2-4 km)	171 (173±45)	54 (60±21)	744 (840±258)	636 (642±207)
ΔC (ppt)	-34	-6	+181	+199
Loss rate in MBL (days ⁻¹)	1.43	1.43	0.12	0.05
F _t (g cm ⁻² s ⁻¹)	-0.0 x 10 ⁻¹²	-0.0 x 10 ⁻¹²	+1.0 x 10 ⁻¹³	+1.9 x 10 ⁻¹³
F _{mbb} (g cm ⁻² s ⁻¹)	-1.1 x 10 ⁻¹²	-0.4 x 10 ⁻¹²	-0.4 x 10 ⁻¹³	-0.7 x 10 ⁻¹³
F _o (g cm ⁻² s ⁻¹)	+1.1 x 10 ⁻¹²	+0.4 x 10 ⁻¹²	-0.6 x 10 ⁻¹³	-1.2 x 10 ⁻¹³
Oceanic source (Tg y ⁻¹) ^b	+125	+45	-8	-14

^aAn entrainment velocity of 0.4 cm s⁻¹ and a mean MBL OH of 1.5 x 10⁶ molec. cm⁻³ is used; ^bAssumes that calculated oceanic flux is globally applicable; ^cMedian mixing ratio (Mean ± 1σ). See text for details.

Table 2: Seawater OVOC concentrations and reservoir estimated by using an air-sea exchange model

Chemicals	H ^a	K _L ^b (cm h ⁻¹)	r _g /(r _g +r _l) ^c (%)	F _o (g cm ⁻² s ⁻¹)	C _l ^d (nM)	Saturation (%)	R ^e	O-reservoir ^f (Tg)
CH ₃ CHO ^g	9.1x10 ⁻³	14.3	36	+1.1 x 10 ⁻¹²	7	800	7	4
C ₂ H ₅ CHO ^g	9.1x10 ⁻³	13.5	39	+0.4 x 10 ⁻¹²	2	800	4	1

CH ₃ OH	2.2x10 ⁻⁴	1.0	91	-0.6 x 10 ⁻¹³	100	94	25	50
CH ₃ COCH ₃	1.5x10 ⁻⁴	3.9	65	-1.2 x 10 ⁻¹³	10	86	2	10

^aDimensionless Henry's Law constants corrected for salt and hydration effects; ^bTotal air-sea exchange transfer velocity; ^cPercent resistance in gas phase; ^dSurface seawater concentrations (nM=10⁻⁹ mol L⁻¹); ^eRatio of the oceanic to the atmospheric burden over the Pacific assuming a 50 m mixed layer depth; ^fGlobal oceanic reservoir assuming R is maintained and mixing ratios in the SH are 80% of NH; ^gFor these aldehydes, a hydrated ion concentration comparable to the free molecule will also be present in seawater.

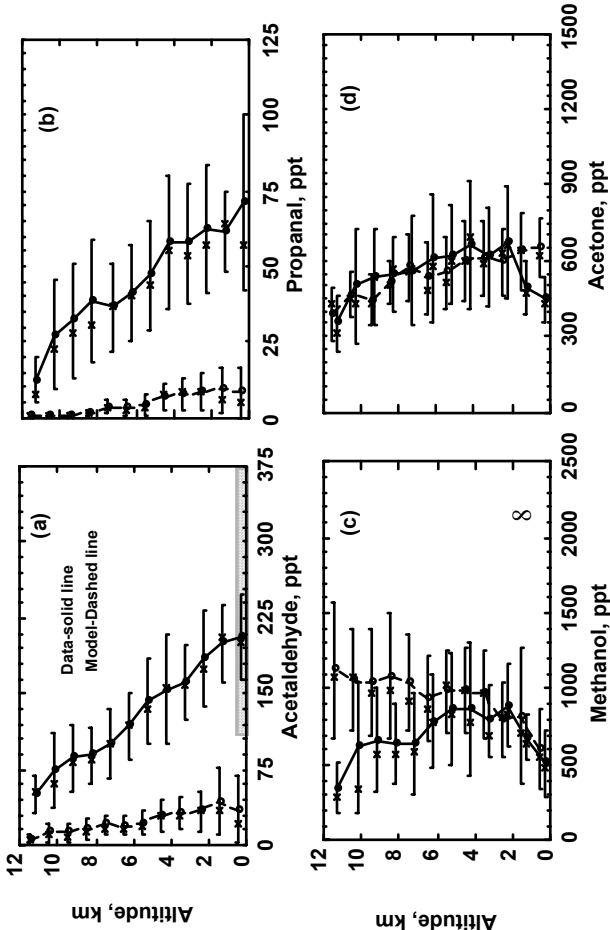


Figure 1: Measured and modeled mixing ratios of selected OVOC. Shaded area in (a) shows the MBL mixing ratio range from many regions of the globe. In the model run oceans provide (in Tg y^{-1}) 13 acetone source, 0 aldehyde source, and 15 methanol sink. Data altitudes are shifted by -0.25 km for clarity. See text for details.